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RECOMMENDED METHODS OF REDUCTION, NEUTRALIZATION, RECOVERY, OR DISPOSAL OF HAZARDOUS WASTE

VOLUME VIII. NATIONAL DISPOSAL SITE CANDIDATE WASTE STREAM CONSTITUENT PROFILE REOORTS. MISCELLANEOUS INORGANIC AND ORGANIC COMPOUNDS

TRW Systems Group

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This volume contains summary information and evaluation of waste management methods in the form of Profile Reports for miscellaneous inorganic and organic compounds. These Profile Reports were prepared for either a particular hazardous waste stream constituent or a group of related constituents. Each Profile Report contains a discussion of the general characteristics of the waste stream constituents, their toxicology and other associated hazards, the definition of adequate management for the waste material, an evaluation of the current waste management practices with regard to their adequacy, and recommendation as to the most appropriate processing methods available and whether the waste material should be considered as a candidate for National Disposal, Industrial Disposal, or Municipal Disposal.

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Organic Compounds
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Antimony Trifluoride
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Contaminated Electrolyte
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Nickel Carbonyl
Perchloric Acid
Acrolein
Dimethyl Sulfate
Pentachlorophenol
Hazardous Wastes

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Volume VIII. National Disposal Site Candidate Waste Stream Constituent Profile Reports - Miscellaneous Inorganic and Organic Compounds

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in:

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

Under Section 212 of Public Law 91-512, the Resource Recovery Act of 1970, the U.S. Environmental Protection Agency is charged with preparing a comprehensive report and plan for the creation of a system of National Disposal Sites for the storage and disposal of hazardous wastes. The overall program is being directed jointly by the Solid and Hazardous Waste Research Laboratory, Office of Research and Development, National Environmental Research Center, Cincinnati, and the Office of Solid Waste Management Programs, Office of Hazardous Materials Control. Section 212 mandates, in part, that recommended methods of reduction, neutralization, recovery, or disposal of the materials be determined. This determination effort has been completed and prepared into this 16-volume study. The 16 volumes consist of profile reports summarizing the definition of adequate waste management and evaluation of waste management practices for over 500 hazardous materials. In addition to summarizing the definition and evaluation efforts, these reports also serve to designate a material as a candidate for a National Disposal Site, if the material meets criteria based on quantity, degree of hazard, and difficulty of disposal. Those materials which are hazardous but not designated as candidates for National Disposal Sites, are then designated as candidates for the industrial or municipal disposal sites.

A. W. Breidenbach, Ph.D., Director
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PROFILE REPORTS ON
THE ANTIMONY FLUORIDES

Antimony Pentafluoride (36), Antimony Trifluoride (43)

1. GENERAL

Introduction

Antimony pentafluoride and antimony trifluoride are included in a combined Profile Report because of similarities in chemistry, toxicology, other hazards and industrial uses.

Antimony Pentafluoride

Antimony pentafluoride is a colorless, hygroscopic, corrosive moderately viscous, oily liquid. The compound has an appreciable vapor pressure at room temperature, and fumes in air, with hydrolysis to HF. The physical and chemical properties of SbF_5 are summarized in the attached worksheet.

The large scale production of SbF_5 is accomplished by the addition of an excess of anhydrous hydrogen fluoride to antimony pentachloride in an all-aluminum apparatus.[1988] The mixture is agitated during the addition of the HF, except for the mid-stage of the reaction, during which intermediate solid chlorofluorides are formed. The anhydrous HF is refluxed over the mixture until all of the chlorine has been displaced as HCl, in accordance with the reaction:

$$SbCl_5 + 5HF \rightleftharpoons 5HCl + SbF_5$$

The HCl is driven off by distillation, followed by the excess HF.

The major uses of antimony pentafluoride are:

(1) the preparation of organic fluorine compounds, either alone or in combination with hydrogen fluoride, iodine pentafluoride, or antimony pentachloride;
(2) the substitution of fluoride for chlorine in chlorinated hydrocarbons;
(3) the formation of complex compounds with other metal salts and halogens;
(4) the preparation of inorganic fluorides by reaction with P_4O_{10}, $MoCl_5$, CrO_2Cl_2, PCl_3, and other similar compounds.

The most important fluorinating agent for industrial fluorinations is hydrogen fluoride in the presence of antimony (V) compounds. Sb (V) is the most useful and most effective catalyst, and SbF_5 is the most effective fluorinating agent.

Antimony Trifluoride

Antimony trifluoride is a white deliquescent crystalline solid. The commercial salt frequently contains antimony oxide or a basic salt. The crystal lattice is molecular in character, although the chemical reactions of the compound are most frequently ionic.[1988] SbF_3 is extremely soluble in water, in which it undergoes a limited hydrolysis. The physical and chemical properties of SbF_3 are summarized in the attached worksheet.

Antimony trifluoride may be prepared by crystallization from a solution of Sb_2O_3 in excess hydrofluoric acid. The more common method of manufacture is by reacting $SbCl_3$ and excess anhydrous HF. Hydrogen chloride is evolved at 0 to 15 C; excess hydrogen fluoride is distilled off at 40 to 50 C; unreacted $SbCl_3$ is removed by extraction with carbon tetrachloride.

The major uses of antimony trifluoride are:

(1) to catalyze fluorination of organic compounds by anhydrous HF;
(2) to manufacture organic chlorofluroides by metathesis;

(3) in the form of the sodium fluoride and ammonium sulfate double salts, in dyeing;

(4) in the manufacture of pottery and porcelains.

The fluorinating power of the antimony fluorides varies from relatively mild antimony (III) fluoride through mixtures of antimony (III) fluoride and antimony (V) chloride to very powerful antimony (V) fluoride. A moderately high degree of selectivity is achieved in the substitution of fluorine for the other halogens by proper choice of antimony fluoride.[2027]

Antimony (III) fluoride is only slightly more active than hydrogen fluoride and behaves similarly when mixed with HF. It will, however, give substitution in a dialkyldichloromethane, in contrast to HF. The order of strengths cited above has been summarized as follows:[2027]

$$SbF_3 < (SbF_3 + SbCl_3) < (SbF_3 + SbCl_5) < SbF_3Cl_2 < SbF_5$$

2. TOXICOLOGY

Human Toxicity

The antimony florides produce physiological responses exhibiting the combined effects of soluble antimony compounds and soluble fluorides. For antimony (V) fluoride (SbF_5), caustic effects similar to those of hydrofluoric acid are superimposed upon the toxicity due to soluble antimony and soluble fluoride compounds.[1492]

Specifically, exposure to soluble antimony compounds causes dermatitis, keratitis, ulceration of the nasal septum,[1492] complaints referable to the nervous system (irritability, sleeplessness, fatigue and dizziness), pneumonitis, fatty degeneration of the liver, a decreased leucocyte count, and damage to the heart muscle.[0766] Symptoms in most cases include intense gastric and intestinal irritation, with epigastric pains, dysphagia, a metallic-like taste, vomiting of blood-stained material, tenesmus, watery diarrhea, rapid pulse, profuse sweating, and spasms of

the muscles of the extremities. In fatal cases, cyanosis, subnormal temperature, delirium and collapse may also occur. A lethal dosage as low as 3 grains, taken in 1-1/2 grain increments over a 24-hr interval has been reported, [2028] but larger doses have been non-lethal.

Chronic poisoning due to ingestion/inhalation of soluble antimony compounds may occur, with symptoms of anorexia, nausea, vomiting, thirst, diarrhea, muscular cramps and cold sweats.[2028]

The TLV for antimony compounds is 0.5 mg/cubic meter.[0766]

The effects of soluble fluorides include nausea and vomiting, salivation, burning, cramp-like abdominal pains, diarrhea, dehydration and thirst, muscle weakness, central nervous depression, cyanosis, shock, weak and thready pulse, shallow unlabored respiration, weak heart tones, paralysis of the muscles of deglutation, carpopedal spasm, spasm of the extremities, and, in extreme cases, death. Anhydrous SbF_5, or highly concentrated solutions, produces burns similar to those of HF; these burns are usually more severe than those from the other mineral acids.[1988] External contact causes severe irritation of the eyes and eyelids,[2023] resulting in prolonged or permanent visual defects or total destruction of the eyes. Inhalation may cause extreme irritation of the respiratory tract, pulmonary inflammation, and congestion. Ingestion causes necrosis of the esophagus and stomach, with the additional symptoms noted above. The skin is burned by SbF_5,[2023] and severely irritated by SbF_3.[1492]

Lethal dosages of 1-1/2 to 2 grams (25 to 30 grains), expressed as F, of soluble fluoride have been reported[1988]; prompt treatment has averted death with much larger quantities.[1988] Chronic fluoride poisoning, reported for other soluble fluorides from exposures to relatively large (but sub-acute) dosages of fluoride over protracted periods, is improbable with the antimony fluorides, since the acute toxic effects due to antimony would supervene at the dosages indicated (ranging from 20 to 80 mg or more of fluoride per day[1988]).

The Federal Water Pollution Control Administration (FWPCA) report on "Water Quality Criteria"[0536] did not establish concentration limits for antimony in public water supplies, although mention was made of potential toxicity.

Aquatic Toxicity

Antimony fluoride has been reported as lethal to fish in concentrations which range from 100 to 200 parts per million.[1988] A dose of 5 mg (injection) was lethal to frogs.[1988]

3. OTHER HAZARDS

Antimony trifluoride and antimony pentafluoride solutions are highly corrosive to most metals, due to the highly acid properties of the salt-water systems. Antimony pentafluoride, anhydrous, corrodes glass, copper and lead,[1492] and attacks paper, wood, rubber, and many plastics.[1988] Neither salt is flammable, but both are easily volatilized, to give toxic fumes.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Great care must be exercised in handling antimony pentafluoride, because of its volatility and hazardous, highly reactive character. A face shield, neoprene gloves, and protective clothing are recommended in the handling of SbF_5.[2023] Material spilled on the skin should be immediately flushed away with large quantities of cold water until all of the compound is removed (up to 4 hours, or until medical attention is obtained), paying particular attention to the skin under the nails. Prompt medical attention is required. Where medical attention is delayed, a mixture of glycerin and magnesium oxide should be applied.[2023] Clothing which has been contaminated should be removed and washed before re-use. If any SbF_5 gets into the eyes, prompt medical attention is absolutely necessary. The eyes should be flushed immediately with cool water for 15 to 30 minutes.[2023] Personnel handling SbF_5 should avoid breathing the vapor.

Antimony pentafluoride is shipped in steel cylinders (1,5,25, and 200 lb SbF_5 content) and, in accordance with Department of Transportation (DOT) regulations, must carry a "Corrosive liquid" white label when shipped in interstate commerce or by boat. The cylinders should be stored outdoors, protected from the weather, or in a well-ventilated room. Exposure to fire or direct heat should be avoided.[2023]

Since antimony trifluoride is a solid, handling hazards are less than those involved with antimony pentafluoride. The same general precautions should, however, be taken in handling SbF_3 as are listed above for SbF_5.

There are no current Department of Transportation or Coast Guard regulations which cover shipment or labeling of antimony trifluoride. Polyetnylene containers are used for shipping the material.

Criteria for acceptable disposal of the antimony fluorides,defined in terms of the recommended provisional limits in the atmsophere, in potable water sources, and in marine habitats, are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
SbF_5	0.005 mg Sb/M^3	0.01 TLV
SbF_3	0.005 mg Sb/M^3	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
SbF_5	0.05 ppm Sb(mg Sb/l)	Chronic toxicity drinking water studies
SbF_3	0.05 ppm Sb(mg Sb/l)	

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

The major use of the antimony fluorides is as catalysts and fluorine carriers in the manufacture of fluorcarbons. The amounts of all fluorides emitted to the environment from the fluorcarbon manufacturing processes are extremely small. Because of the highly toxic and corrosive nature of the feed and catalyst materials, extreme care is taken to control spills and leakage. All product streams are scrubbed to meet purity

specifications; the unreacted HF is removed as solid CaF_2 and disposed of in that form.[1688] There are no gaseous effluent streams. For these reasons, current practices for prevention of antimony fluoride waste discharge from the fluorocarbon manufacturing processes are deemed completely satisfactory.

There are no procedures reported for the disposal of small quantities of the antimony fluorides, with the exception of advice not to use water on fires involving antimony pentafluoride.[0094]

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Manufacturing process effluent streams containing the antimony fluorides can best be handled at the sites where they originate by the continuation of current, acceptable disposal processes. Small contaminated or surplus quantities of antimony trifluoride and antimony pentafluoride should either be returned to the manufacturers for reprocessing, or disposed of at National Disposal Sites. The disposal method to be employed at the National Disposal Sites will require development. A proposed disposal process is to combine Methods 27d and 11 of the Manufacturing Chemists Association Laboratory Waste Disposal Manual.[0095] Briefly stated, the disposal concept is as follows: Dissolve the antimony fluoride in the minimum quantity of dilute hydrochloric acid. Saturate with hydrogen sulfide. . Filter, wash and dry the antimony sulfide precipitate; sell the precipitate to a primary antimony metal producer. Air strip the filtrate of dissolved H_2S,passing the effluent air into a controlled incineration device, equipped with a lime scrubber. React the stripped filtrate with an excess of lime; evaporate to dryness, and dispose of the lime-CaF_2-$CaCl_2$ mixture by land burial.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Antimony Trifluoride

IUC Name Antimony (III) Fluoride

Common Names Antimonous Fluoride

Structural Formula

SbF_3

Molecular Wt. 178.75 Melting Pt. 292 C (2) Boiling Pt. 376 C (3)*

Density (Condensed) 4.379(s) @ 20.9 C Density (gas) _____ @ _____

Vapor Pressure (recommended 55 C and 20 C)

3mm @ 17 C(1) 107mm @ 62 C(1) _____ @ _____

Flash Point _____ Autoignition Temp. _____

Flammability Limits in Air (wt %) Lower _____ Upper _____

Explosive Limits in Air (wt. %) Lower _____ Upper _____

Solubility

Cold Water 384.7g/100g @ 0 C (1) Hot Water _____ Ethanol _____

Others: _____

Acid, Base Properties Undergoes limited hydrolysis with water to form HF.

Highly Reactive with _____

Compatible with Glass and steel, if dry.

Shipped in Glass containers or steel drums

ICC Classification None Coast Guard Classification None

Comments SbF_3 is used as a fluorinating agent in the Swarts Reaction. Forms salts of the type K_2SbF_5. Na_3SbF_6 with metal fluorides. Double salts are used in dyeing. Also used in the manufacture of pottery and porcelains.

References (1) 1988
(2) 1433
(3) 1492

*Sublimes @ 319 C

HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. Name Antimony Pentafluoride

IUC Name Antimony (V) Fluoride

Common Names Antimony Pentafluoride

Structural Formula

SbF_5

Molecular Wt. 216.74 Melting Pt. 8.3 C (1) Boiling Pt. 142.7 C (1)

Density (Condensed) 3.145 (liq.) @ 15.5 C (1) Density (gas) _____ @ _____

Vapor Pressure (recommended 55 C and 20 C)

4.3mm @ 25 C (4) 18mm @ 50 C (1) 170mm @ 100 C (1)

Flash Point _____ Autoignition Temp. _____

Flammability Limits in Air (wt %) Lower _____ Upper _____

Explosive Limits in Air (wt. %) Lower _____ Upper _____

Solubility

Cold Water Sol., with reaction. Hot Water _____ Ethanol Reacts

Others: _____

Acid, Base Properties Solution in water strongly acid.

Highly Reactive with water, to form $SbF_5.2H_2O(s)$. Corrodes glass, copper and lead. (3) Attacks skin, paper, wood, rubber. (1)

Compatible with steel when dry. May be stored in aluminum when dry.

Shipped in 1, 5, 25, 200 lb. steel cylinders. (2)

ICC Classification Corrosive liquid; white label Coast Guard Classification Corrosive liquid; white label.

Comments Fumes in air, with hydrolysis to HF (2). Forms $HSbF_6$ with HF; many metallic fluoroantimonate salts are known. Used as fluorinating agent. Reacts with P_4O_{10}, $MoCl_5$, CrO_2Cl_2 and organochlorine compounds to yield fluoro-compounds. Hygroscopic, corrosive, moderately viscous liquid. Forms addition compounds with halogens and many organics.

References (1) 1988 (4) 2023
(2) 1996
(3) 1492

PROFILE REPORT

Chlorine (105)

1. GENERAL

Liquid chlorine is a clear amber-colored liquid about 1.5 times as heavy as water. Gaseous chlorine is greenish-yellow, about 2.5 times as heavy as air. Chlorine has a disagreeable and suffocating odor with an irritating effect on the nose and throat. Chlorine is not flammable. It is shipped as a liquid in steel cylinders under its own vapor pressure of about 85 psig at 70 F.

In 1969, 9.5 million tons of chlorine were produced[1563] with an increase in 1972 to 10.6 millions tons projected. Over 99.5 percent was produced electrolytically with the remainder accounted for by various chemical processes. The diaphragm and mercury electrolytic cells generated approximately 65 percent and 30 percent respectively; molten salt cells produced slightly less than 5 percent. In 1969 it was estimated that 78,200 tons of chlorine were emitted into the atmosphere.[1563] A summary of the chlorine emissions is presented below:

SOURCE	CHLORINE EMISSIONS, TONS
Chlorine Manufacture	47,000
Hydrochloric Acid Manufacture	800
Chemical and Industrial Processes	
Organic Chlorinations	8,500
Pulp Bleaching	18,000
Metallurgical Processing	2,000
Bleach Manufacture	900
Miscellaneous	1,000

The physical/chemical properties of chlorine are summarized in the attached worksheet.

2. TOXICOLOGY

Human Toxicity

Chlorine is an extremely powerful vessicant and respiratory irritant. Its action is that of a severe irritant, rather than as a specifically toxic agent. High concentrations of chlorine cause pulmonary edema which may have fatal termination. Inhalation of lower concentrations causes coughing, smarting of the eyes, a general feeling of discomfort in the chest, nausea, and vomiting. The effects of different concentrations of chlorine gas[1301] are shown below.

EFFECT	CHLORINE, ppm
Min. concentration detectable by odor	3.5
Min. concentration causing throat irritation	15
Min. concentration causing coughing	30
Min. concentration causing slight symptoms after several hours	1
Max. concentration that can be breathed for one hour without damage	4
Concentration dangerous in 30 minutes	40-60
Concentration likely to be fatal after a few deep breaths	1000
Threshold limit value for 8-hour exposure (ACGIH)	1

Liquid chlorine causes severe irritation and blistering of the skin.

Toxicity Toward Aquatic Life

The toxicity of chlorine solutions in water is usually not considered a problem. Dissolved chlorine reacts rapidly with organic and other oxidizable substances in natural streams and chlorine escapes from water at pH < 7 at a rather rapid rate. Some species of fish are sensitive to dissolved chlorine, i.e., tropical fish in home tanks are sensitive to 0.1 ppm of chlorine. Limits for residual chlorine in effluents to streams in various states are usually set at 0.5 to 1.5 ppm.[1562]

Toxicity Toward Plant Life

The effect of various concentrations, 300 to 4,500 $\mu g/m^3$ (0.1 to 1.5 ppm) of chlorine gas on 26 different species of plants was studied.[0625] The most common symptoms of chlorine poisoning were necrosis and bleaching of the foliage, which occurred a day or two after the chlorine exposure. Bleaching of the leaves was a typical symptom which developed from exposure to low concentrations of chlorine.

3. OTHER HAZARDS

Moist chlorine is very corrosive to all of the common materials of construction except high silica iron, monel, Hastelloy C, silver, and the noble platinum metals. At low pressures wet chlorine can be handled in chemical stoneware, glass, procelain, and certain plastics.

Although chlorine is nonflammable, it is capable of supporting the combustion of many materials including hydrogen, the reactive metals and many organic compounds. Chlorine reacts with most non-metallic elements, sometimes very rapidly. With basic materials chlorine reacts to form chlorides and hypochlorites. Chlorine has a great affinity for combined hydrogen to yield hydrogen chloride. Many organic compounds are extremely reactive, yielding chlorinated organic derivatives and hydrochloric acid.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Adequate procedures for safe handling, transportation and storage of chlorine are provided by Matheson in the Gas Data Book.[1301] This document provides recommended procedures for equipment design, employee safety, design of shipping and storage containers, federal classification and regulations, emergency rescue, first aid and material specifications.

Chlorine is Department of Transportation (DOT) classified as a non-flammable compressed gas taking a green label. It is shipped in 100- and 150-lb steel cylinders, single unit tank cars of 30,000 pounds and multi-unit tank cars of 15 one-ton units.

Disposal/Reuse

A definition of acceptable criteria for the disposal of chlorine also takes into account acceptable criteria for the release of chlorine to the environment. Current practice in chlorine disposal usually involves: (1) recycling, (2) recovery, (3) alkaline scrubbing, or (4) venting. The safe disposal of chlorine is defined in terms of the recommended provisional limits for chlorine in the atmosphere, in potable water sources, and in marine habitats. These are:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Chlorine	0.03 mg/M^3	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Chlorine	0.15 mg/l	Stokinger and Woodward Method

Contaminant in Marine Habitats	Provisional Limit	Basis for Recommendation
Chlorine	0.003	0.01 Fish Toxicity

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Litton Systems Inc. has provided a Technical Report[0625] which identifies, by process, the sources of chlorine emissions and estimated the quantities of chlorine emitted. A summary of these emissions are presented in Section 1. Current disposal practices for the various sources are briefly described in the following paragraphs together with recommendations as to their adequacy.

Chlorine Manufacture

Potential sources of chlorine emissions from electrolytic chloro-alkali plants and approximate quantities emitted[1563] are as follows:

SOURCE	EMISSION*, $lbCl_2$/ton Cl_2 PRODUCED	CONCENTRATION
Cell Operation	0.1	0-100%
Acidifying, air blowing, and vacuum treating depleted brine	7.5 to 10	0-10%
"Blow Gas" from chlorine liquefaction process	2 to 16	20-50%
Vents from storage tanks, process transfer tanks, tank cards, and shipping containers	.1 to 6.0	0-100%
Leaks and spills due to corrosion, wear and accidents	Variable	0-100%

*Some emissions are recovered

In all cases, chlorine emissions can be reduced to virtually zero by recovery and/or alkaline scrubbing, when the recovery and scrubbing systems are properly designed and used. The particular technique used for controlling a chlorine emission source depends upon the concentration of chlorine in the vent stream, the quantity of chlorine emitted and the markets for possible by-products such as hydrogen chloride, sodium hypochlorite, or chlorobenzene.

If the chlorine content of the effluent stream is greater than 10 percent, recovery as chlorine is economical and is usually employed.

Alkaline scrubbers are normally used for dilute streams such as those resulting from air blowing of depleted brine. Packed bed, counter-current flow scrubbers are commonly used for more concentrated streams.[1563]

Chemical and Industrial Processes

Organic Chlorination. Approximately 80 percent of the chlorine produced is used in the manufacture of organic chemicals. In some processes, the chlorinated compound is an intermediate, while in other processes chlorine is a part of the final product. In most modern organic chlorination processes, the exit gas streams are recycled and only low levels of chlorine are emitted in purge gas streams. Control of emissions from these vent streams is accomplished by the use of alkaline scrubbing systems.

Paper Pulp Bleaching. During 1969, approximately 1,400,000 tons of chlorine were used by the pulp and paper industry for bleaching.[1563] Without vent gas control systems, chlorine emissions are about 18 to 42 lb per ton of chlorine used. Cerstle and Timothy[1563] indicates that the alkaline scrubbers used typically remove only 96 percent of the chlorine emissions. This indicates that the scrubbers in use are probably underdesigned for peak load service.

Manufacture of Bleaches and Sanitizing Agents. In 1969, approximately 180,000 tons of chlorine were used in the manufacture of bleaches and sanitizing agents such as liquid bleach (sodium hypochlorite solution), bleach liquor (lime bleach), chlorinated tri-sodium phosphate, chlorine dioxide, chlorinated isocyanates and chloroamines.[1563] Under normal operating conditions for the manufacture of these compounds, little or no chlorine is emitted. However, process upsets will occasionally occur and the batch may decompose to liberate chlorine. Scrubbers, although required to take care of these upsets, are not normally used.

Other Uses. Other significant uses of chlorine include non-ferrous metallurgical processing, water and sewage treatment, and production of metal chlorides and reactive metals.

Approximately 30,000 tons per year of chlorine are consumed in aluminum and other metal production and treating processes.[1563] The chlorine is used to prepare metal chlorides, fluxes for degassing and purification of the metal.

In metal smelting and processing little or no chlorine is emitted; the pollution results from the evolution of metallic chloride fumes such as zinc, magnesium, or aluminum chlorides and the evolution of hydrogen chloride.

Chlorination is the basic process in water and sewage treatment. In 1969, 330,000 tons of chlorine were used for water treatment with large quantities being used to treat sewage at some stage of the disposal process.[1563] Since most chlorine used in water treatment ends up as a chloride salt, especially in alkaline water, chloride emissions from water treatment are negligible. When waste streams, such as those from plating shops, are overchlorinated, the excess chlorine is customarily removed by treatment of the waste stream with sodium acid sulfite.

Abatement Processes

The processes recommended for abatement of gaseous chlorine emissions and disposal of the recovered chlorine are water scrubbing, followed by alkali scrubbing, with recycle of chlorine stripped by heating from water solution, and carbon reduction of the hypochlorite bleed off from alkali scrubbing. These are discussed in the following paragraphs.

Water Scrubbers. If water scrubbers are used for effluent control, the chlorine-containing vent gas is passed countercurrent to the water stream in a tower filled with ceramic packing. Characteristic water scrubber reductions in vent gas are from an initial 15 percent chlorine by volume to an effluent gas containing 15 to 30 g/m^3 (0.5 to 1.0 volume %) of chlorine.[0625] Common practice is either to pass the tail gases from water scrubbers through more efficient alkali scrubbers, or to tall stacks for disposal. The chlorine-rich scrubber solution is heated so that the chlorine may be stripped and recovered. An alternate method[0625] of treatment is to pass the chlorine-rich water over iron filings or activated charcoal, or to add ferrous chloride solution. The result is an oxidation-reduction reaction that converts the chlorine to the noninjurious chloride ion. If ferrous chloride solution is used, additional iron filings (scrap iron) are employed

to reduce a portion of the ferric chloride formed to ferrous chloride. The bulk of the ferric chloride produced is sold. Used alone, water scrubbing does not reduce chlorine emissions to permissible levels. It is therefore recommended that water scrubbing be followed by scrubbing with alkaline solution.

Alkaline Scrubbers. Contact of chlorine with alkaline solutions, usually caustic or lime, produces an effluent gas with a lower residual chlorine concentration than can readily be attained by water scrubbing.[0625] The reaction products are sodium or calcium hypochlorite, and sodium or calcium chloride. The major disadvantages of this method are the cost and the difficulty of disposing of the hypochlorite solution. The hypochlorite solution is either sold, used in another part of the plant, treated with carbon to reduce the hypochlorite to chloride ion, or disposed of by dumping into rivers and streams. The last practice is not recommended. If properly designed, the alkaline scrubbers, used alone or after a water scrubber, can reduce the chlorine concentration of effluent streams to below 1 ppm.

Carbon Tetrachloride Scrubbers. The advantages of using carbon tetrachloride as an absorbent are that its absorbing capacity for chlorine gas is 10 to 12 times greater than water and the recovery of chlorine is complete.[0625] However, losses of carbon tetrachloride have been reported under uncontrolled conditions to be as great as 30 lb per ton of recovered chlorine. The carbon tetrachloride scrubber is operated at 100 psig and the chlorine stripped by reducing the pressure to 35 psi. A condenser is required to remove vaporized carbon tetrachloride before compression and liquefaction of the stripped chlorine.[0625]

Silica Gel Absorption. Small quantities of chlorine are collected on silica gel; the absorbed chlorine is recovered[0625] by heating. Though satisfactory, this method is not widely used because of excessive costs when large quantities of chlorine must be recovered.

Reaction with Sulfur. High strength vent gases are infrequently reacted with sulfur to form sulfur chlorides. This method is not recommended unless there is a specific market for the sulfur chlorides. The disposal of sulfur chlorides is more difficult than the disposal of chlorine.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

It is anticipated that systems to handle the great majority of the chlorine containing effluents generated in the manufacture of chlorine and in process industries will continue to be located at the source of effluent generation rather than at National Disposal Sites in view of the economics involved. However, some capacity to process chlorine and chlorine-contaminated wastes with minimum environmental impact is required at National Disposal Sites for the following requirements:

(1) Occasional tank-car or smaller lots of liquid chlorine which for reasons are required to be disposed of in a safe, pollution-free manner.

(2) Secondary gas streams generated within the National Disposal Site as a result of processing other wastes (e.g., from disposal of interhalogen compounds).

It is suggested that the following unit operations will be required for these purposes at National Disposal Sites:

(1) Water Scrubbing and Stripping Units

Chlorine-containing gas will be stripped of most of its chlorine content by passing the gas stream countercurrent to a water stream in a tower filled with ceramic packing. Chlorine is stripped from the recirculating liquor by heating the absorption tower exit stream, and using the standard drying, refrigeration, and compression systems for liquefaction of the chlorine. The collected chlorine is then available for use at the National Disposal Site, or for sale. The tail gas from the water scrubber is treated as noted under (2) below.

(2) Alkaline Scrubbers

The vent gas from the water scrubbers above must be followed with an alkaline scrubber to remove the residual chlorine. In some cases it will be more convenient to convert chlorine present at low concentrations in waste gas streams to sodium hypochlorite in an alkaline scrubber, without prior use of the water scrubbers. Any hypochlorite made can be used in cyanide disposal processes at the National Disposal Sites.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Chlorine (105)

IUC Name Chlorine

Common Names

Structural Formula

Cl_2

Molecular Wt. 70.906 Melting Pt. -101±2°C Boiling Pt. -34.05 C

Density (Condensed) 1.468 g/cc @ 0 C Density (gas) 3.214 g/l @ 0 C

Vapor Pressure (recommended 55 C and 20 C)

85.46 psia@ 70 F 151.12 psia @ 105 F 174.69 psia @ 115 F

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 0.8% at 10 C Hot Water 0.54% at 30 C Ethanol Reacts

Others: Alkaline Water

Acid, Base Properties Water solutions are slightly acid.

Highly Reactive with Wet-reacts with most metals. Reacts wet or dry with many organic compounds.

Compatible with With most metals when dry.

Shipped in 100, 150-pound steel cylinders, 15-1 ton units.

ICC Classification Nonflammable gas Coast Guard Classification Nonflammable gas

Comments Critical Temperature 44.0 C
Critical Pressure 76.1 alm

References (1) 1301

PROFILE REPORT

Contaminated Electrolyte (118)

1. GENERAL

All elements which could normally make up a contaminated electrolyte residue are covered in one of the following Profile Reports:

Cadmium Cyanides (84)

Chrome (113)

Copper Cyanides (120)

Cyanides (129)

Nickel Cyanide (295)

Silver Cyanide (370)

Zinc Cyanide (457)

Hexavalent Chromium - (21), (22), (343), (345), (379), (386)

With the one exception of chrome, all of the above are recommended as candidate waste stream constituents for National Disposal Sites.

PROFILE REPORT

Fluorine (200)

1. GENERAL

Fluorine is a highly toxic and corrosive pale yellow gas, with a sharp, penetrating, and characteristic odor. It is shipped in cylinders as a non-liquified gas in commerce, but may be shipped as a cryogenic liquid for rocket propellant use. Fluorine is the most powerful oxidizing agent known, reacting with practically all organic and inorganic substances with the exception of the inert gases, metal fluorides in their highest valence state and a few pure completely fluorinated organic compounds. Even the latter may burn in a fluorine atmosphere if contaminated with a combustible material or if subjected to high flow rates of fluorine or excessive mechanical forces. Hydrogen and fluorine combine with extreme violence forming hydrogen fluoride. Oxygen does not ordinarily react with fluorine, but two oxygen fluorides, OF_2 and O_2F_2 are known.[1300]

Fluorine is now manufactured by electrolysis of a liquid mixture of potassium fluoride and hydrogen fluoride. It is used as a rocket propellant and for the production of uranium hexafluoride, sulfur hexafluoride, boron trifluoride and the metal fluorides, silver difluoride, cobalt trifluoride and manganese trifluoride. The metal fluorides are used in the preparation of fluorocarbons.[1301]

Fluorine will not usually appear in a waste stream unless there is an accidental excess over the stoichiometric quantity required by a preparation reaction. However, fluorine frequently becomes contaminated with volatile fluorides such as silicon tetrafluoride, carbon tetrafluoride, and hydrogen fluoride and carbon dioxide. Though the impurities can be removed, it is sometimes desirable to dispose of the contaminated fluorine. It also may be desirable to dispose of excess fluorine on hand at the Department of Defense facilities.

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The chemical and physical properties of fluorine are summarized in the attached worksheet.

2. TOXICITY

Fluorine is severely toxic in both liquid and gaseous forms. The primary effects are local discomfort and irritation to the eyes, lungs and skin. Industrial experience and animal studies indicate that acute exposure causes pathological lung changes prior to liver damage, kidney damage, or significant biochemical, hematological, weight, or skeletal changes. Because of the extreme toxicity and high probability of permanent injury from exposure, all affected persons should be removed from the contaminated area, and referred to a physician after local emergency treatment in all cases. Emergency treatment procedures are the same as those listed for Chlorine Trifluoride.[106] The Threshold Limit Value (TLV) is 0.1 ppm (0.2 mg/M^3). The odor of fluorine is detectable at 0.011 to 0.014 ppm.[1300] Therefore, there is little danger or hazard to personnel from undetected or insidious leaks. Emergency exposure limits are as follows:[1300]

Time	Concentration
10 min	15 ppm
30 min	10 ppm
60 min	5 ppm

3. OTHER HAZARDS

If fluorine is allowed to react with hydrogen, such as in a hydrogen-fluorine rocket engine, or with a hydrocarbon, hydrogen fluoride is produced. Hydrogen fluoride is less toxic than fluorine; the Threshold Limit Value is 3 ppm, thirty times that of fluorine. Hydrogen fluoride is also formed when fluorine reacts with water. The rate at which water and fluorine react increases with the concentration of fluorine.

The reaction of fluorine with many metals is slow at room temperature and often results in the formation of a metal fluoride film.[1154] This film retards further attack in the case of certain metals such as brass, iron, aluminum, magnesium and copper. Hence, these metals are quite satisfactory for handling fluorine at room temperatures. Nickel and monel are by far the best materials to use at high temperatures.

Fluorine is a highly reactive oxidizing agent. As such, it must be considered a fire hazard. It reacts with many substances not normally considered combustible, such as sand and glass at elevated temperatures, and asbestos at room temperature. High concentrations of gaseous fluorine, as well as the liquid itself, will spontaneously initiate combustion with an inflammable material.

4. DEFINITION OF WASTE MANAGEMENT PRACTICES

Handling, Storage, and Transportation

Adequate procedures for the safe handling, transportation and storage of fluorine are described by JANAF,[1300] Hazards Working Group, by F. S. Cakle,[1154] and in the military specification for fluorine, MIL-P-27405,[1503] June 28, 1968. Liquid fluorine may be shipped, but there are no published regulations regarding the shipment of liquid fluorine. Insulated tank trucks have been developed and used under special DOT permits (DOT SP-1479, 1956). Refrigeration is achieved and maintained by using a liquid nitrogen jacket or cooling coils. Gaseous fluorine is packaged, shipped and stored in DOT approved, seamless, high pressure, returnable steel cylinders (Department of Transportation Specification 3AA 1000). Gaseous fluorine is classified by the ICC as a flammable compressed gas and is shipped under a red gas label.

Disposal/Reuse

If fluorine becomes contaminated at the manufacturer, it is either purified and collected or it is fed to a reactor making a fluoride.[1304] However, if disposal of excess or contaminated fluorine (normal contaminants

are volatile fluorides such as carbon tetrafluoride and silicon tetrafluoride, carbon dioxide and hydrogen fluoride) is to be accomplished at another site, any definition of acceptable criteria must include processes for disposal of compounds formed during treatment of fluorine. Except for liquid fluorine (none is known to be in storage) fluorine can be transported to National Disposal Sites in ICC approved cylinders that are used for its storage.

The safe disposal of fluorine is defined in terms of the recommended provisional limits in the atmosphere, in potable water and in marine habitats. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis of Recommendation
Fluorine	0.001 ppm	.01 TLV
Contaminant in Water		
Hydrogen fluoride (as F_2/H_2O reaction product	0.10 ppm	(Stokinger and Woodward Method)

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

The processing options for the disposal of fluorine in the gaseous state are briefly described in the following paragraphs together with recommendations as to adequacy. Detailed discussions of the processing operations are presented in the referenced fluorine disposal reports.

Option No. 1 - Venting

JANAF[1300] recommended disposal of residual fluorine from storage tanks or cylinders by venting slowly as a gas. This is not considered a satisfactory method.

Option No. 2 - Burning With Fuel

In addition to venting, JANAF[1300] recommends burning residual fluorine from storage tanks or cylinders by means of a fluorine-hydrocarbon-air burner followed by a caustic scrubber and stack. The caustic scrubber solution is then treated with lime. Large quantities are disposed of by firing in an actual rocket motor and treatment of the exit gases with lime to remove the hydrogen fluoride. These two combustion techniques are usually considered satisfactory.

Option No. 3 - Reaction With a Charcoal Bed

The classic fluorine disposal unit for small quantities is a charcoal bed of 3/8-in. charcoal bits.[1154] The product of the reaction is carbon tetrafluoride a chemically inert and relatively nontoxic compound.[1300] The carbon tetrafluoride produced is usually vented. The charcoal disposal system has proven successful for quantities up to 30 lb of fluorine in approximately 3 min (600 lb per hour). Continuous operation requires a number of parallel disposal reactors. Approximately 17 lb of charcoal is required to treat 100 lb of fluorine. This method has been widely used and can be considered satisfactory for fluorine disposal.[1414] If the fluorine is contaminated with large quantities of hydrogen fluoride, the carbon will initially absorb it and then the hydrogen fluoride is released as the charcoal is consumed. If highly contaminated with hydrogen fluoride, the charcoal reactor must be followed by a limestone bed to remove the hydrogen fluoride. If silicon tetrafluoride is present in large quantities, the charcoal reactor must be followed by a caustic scrubber. This method is satisfactory for the disposal of contaminated fluorine.

Option No. 4 - Discharge into a Water Spray

Fluorine has been disposed of by discharge into a water spray which produces hydrogen fluoride as a product.[1154] The water then was treated with lime to remove the fluorides. The use of this method may result in an explosion, and is therefore not recommended.

Option No. 5 - Absorption by a NaOH, Na_2CO_3, or $NaHCO_3$ Solution

Small quantities of fluorine have been treated in the laboratory by passing the fluorine diluted with nitrogen through a solution of NaOH, Na_2CO_3 or $NaHCO_3$.[1154] This method offers no apparent advantage over the charcoal reactor and, further, the passage of fluorine through NaOH solution produces some oxygen difluoride, a highly toxic material. This method is not recommended.

Option No. 6 - Reaction With Sodium or Calcium Chloride

Vapors of fluorine passed through a reactor tube filled with dry sodium or calcium chloride convert fluorine quantitatively to chlorine.[1304,1154] The chlorine product is recovered by absorption in a caustic scrubber. The resulting sodium hypochlorite can be used for the treatment of wastes, or stored. This method is satisfactory and can be used if desired.

Option No.7 - Treatment With Steam

Steam in a 300 to 1,000 percent excess is used at 500 F to treat fluorine.[1154] This method produces hydrogen fluoride, and has only limited use since a limestone bed is also required.

Option No. 8 - Reaction With Silicon Carbide

Fluorine has been destroyed by treatment with silicon carbide packed in an aluminum tube 24 ft long and 2 in. in diameter. The reaction product is silicon tetrafluoride which requires treatment by a caustic scrubber.[1154] This method has not found wide acceptance and is not recommended.

The dispositions of compounds formed by the various alternative disposal processes and of probable fluorine contaminants are as follows:

Contaminant and Source	Disposition
Hydrogen fluoride (gas from combustion or reaction with water)	React with lime or limestone. Place calcium fluoride formed in land fill (see Profile Report on hydrogen chloride [217])
Carbon tetrafluoride (gas from carbon or hydrocarbon burning)	Vent
Chlorine (gas from reaction with sodium chloride)	Scrub with caustic solution (see Profile Report on chlorine [105])
Silicon tetrafluoride (gas impurity in fluorine which does not react in the charcoal bed disposal process)	If large amount, scrub with caustic solution
Carbon dioxide (gas impurity in fluorine as above)	Vent

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

It is recommended that National Disposal Sites have a unit operation capable of handling fluorine and interhalogen compounds. The recommended method for fluorine is Option No. 3, Reaction with a Charcoal Bed, but Option No. 2, Burning with Fuel, can be used. Option No. 3 is recommended because the method can be used for disposal of both fluorine and the interhalogens, and because there is adequate engineering data for construction of a disposal unit for fluorine.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Fluorine (200)

IUC Name Fluorine

Common Names

Structural Formula

F_2

Molecular Wt. 38.00 Melting Pt. -219.02 C Boiling Pt. -188.13 C

Density (Condensed) 1.90g/cc @ -227 C Density (gas) 1.3 @ 0 C

Vapor Pressure (recommended 55 C and 20 C)

19.7 psia @ -300 F 164.7 psia @ -250 F 794.7 psia @ -200 F

Flash Point - Autoignition Temp. -

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water reacts Hot Water reacts Ethanol reacts

Others: reacts with most

Acid, Base Properties

Highly Reactive with Almost all materials upon heating

Compatible with liquid N_2 and liquid O_2[1]; can be contained in copper, stainless steel, monel, nickel, brass, aluminum

Shipped in pressure tanks

ICC Classification liquid - none flammable - gas DOT Spec 3AA1000 Coast Guard Classification

Comments TLV 0.1 ppm
Critical pressure 809.7 psia
critical temperature -128.65 C

References (1) 1300

PROFILE REPORT

Nickel Carbonyl (293)

1. GENERAL

Nickel carbonyl, $Ni(CO)_4$, is a colorless to straw yellow liquid. Extremely small vapor concentrations in air are very toxic.

The primary processes which utilize the material are the basic Mond process for the refining of nickel (Figure 1) or the improved pressure carbonyl process (Figure 2). In both of these cases the reaction which "gives wings to a heavy metal", is readily reversible. The carbonyl molecule decomposes to nickel metal and carbon monoxide at temperatures in the 300 to 600 F range:

$$Ni + 4\ CO \xrightarrow{120\ F} Ni(CO)_4$$

$$Ni(CO)_4 \xrightarrow{450\ F} Ni + 4\ CO$$

An examination of the flowsheets (Figures 1 and 2) show how this reaction is utilized for the refining of nickel. The carbon monoxide and the residual nickel carbonyl is recycled for further extraction purposes. Thus the only concern, and a very real one because of the toxicity of the nickel carbonyl, is leakage from the system.

Other processes which utilize nickel carbonyl take advantage of the decomposition reaction to remove the hazard by running the waste gas stream through a flame or decomposition furnace, collecting the fine nickel (a suspected carcinogen) and wasting the carbon monoxide to the atmosphere.

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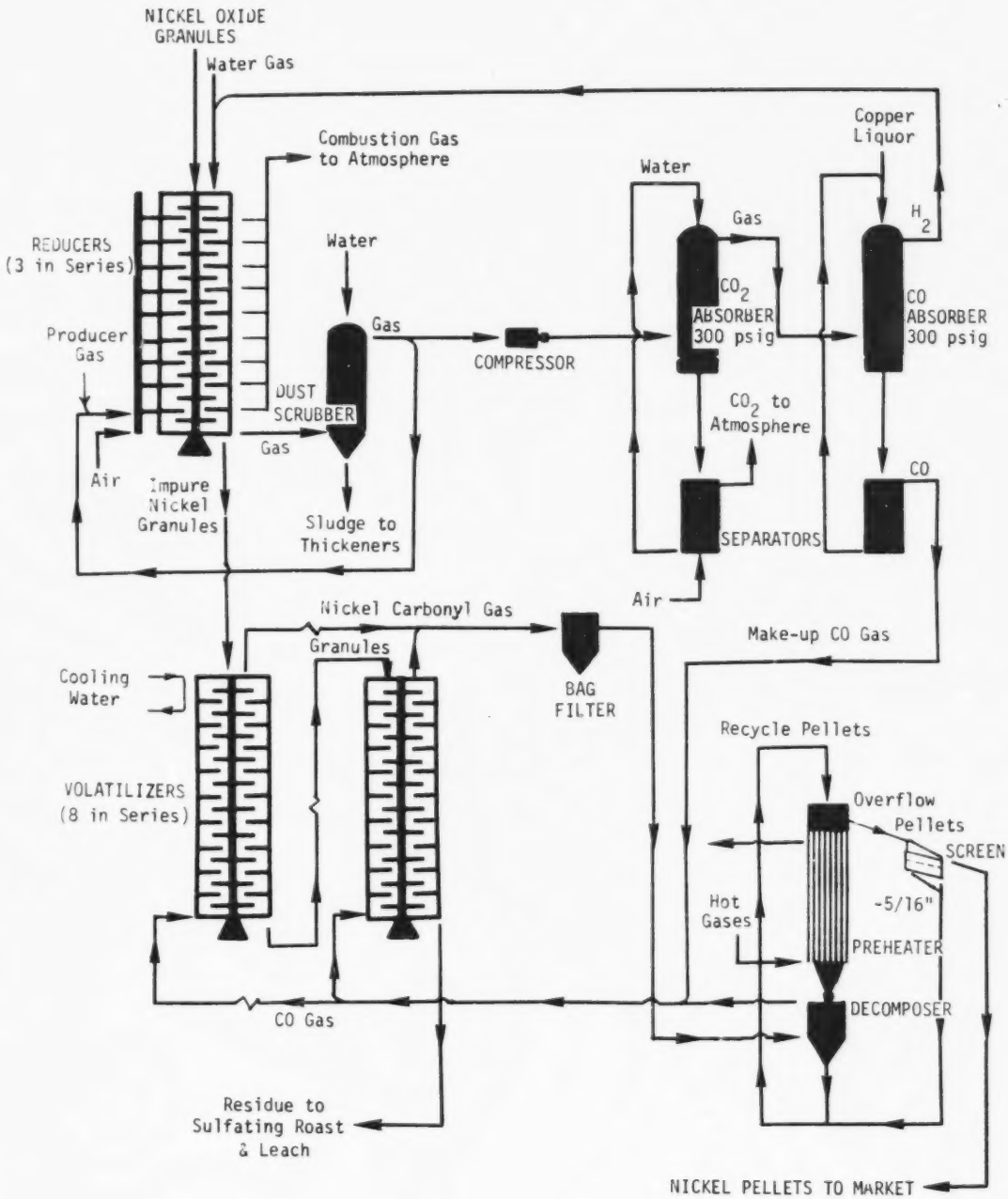

Figure 1. Flowsheet of Atmospheric pressure carbonyl process at Clydach

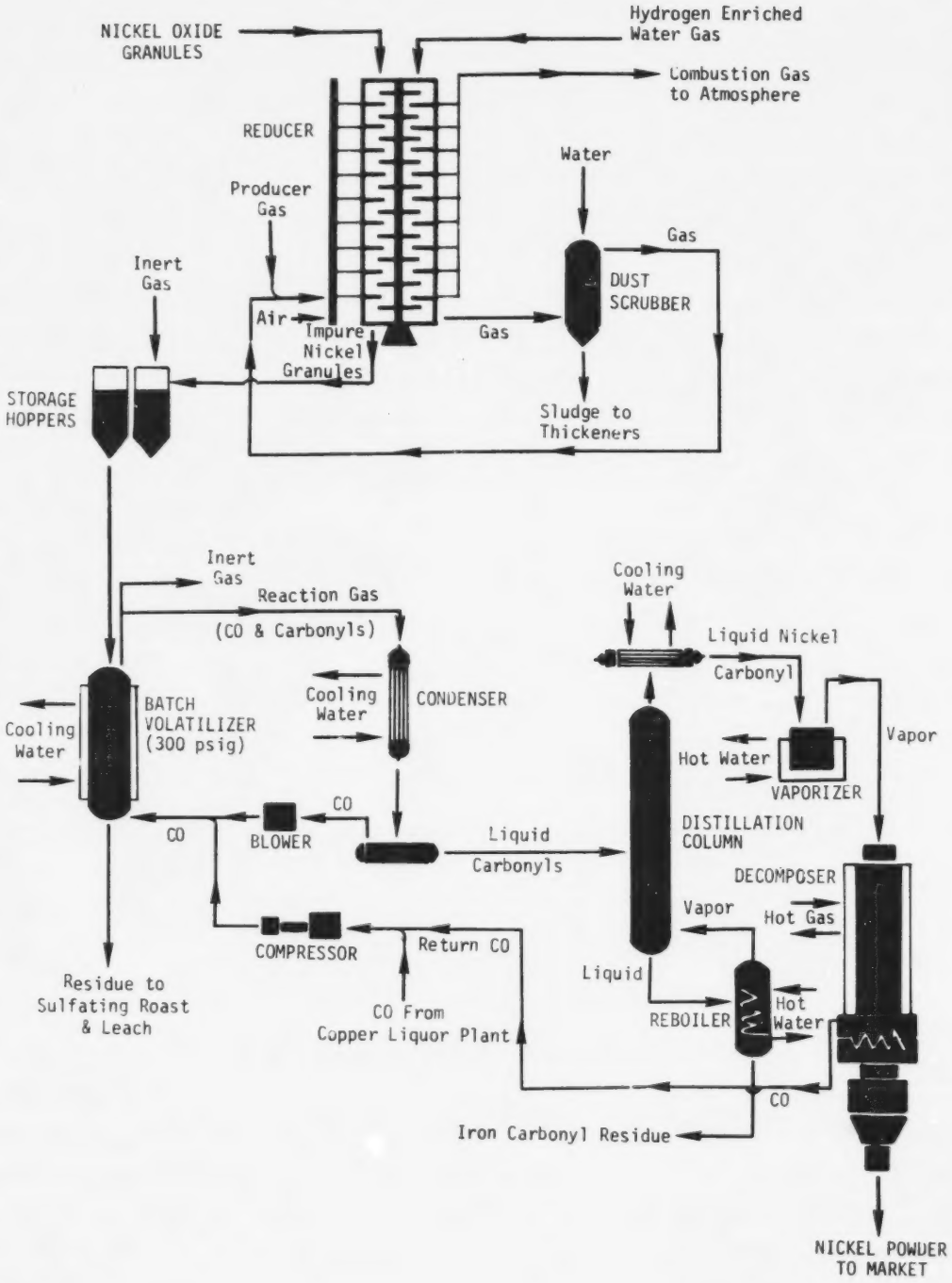

Figure 2. Flowsheet of medium pressure carbonyl process at Clydach

2. TOXICOLOGY

Human Toxicity

The recommended ACGIH Threshold Limit Value (TLV) for $Ni(CO)_4$ is 0.001 ppm in air (0.007 mg/cubic meter) because of the extremely toxic inhalation effects of this material. Exposure results in giddiness and headache accompanied at times by rapid shallow breathing and vomiting. Exposure to fresh air brings relief of symptoms. In a period from 12 to 36 hours after exposure the symptoms recur along with other signs of disturbance of the central nervous system. Death occurs in fatal cases between 4 and 11 days.

3. OTHER HAZARDS

Nickel carbonyl/air mixtures are ignitable and explosive in a wide range. The range lies between 3 and 34 percent volume in air. It is autoigniting at contact with oxygen in the air. Based on these properties it is impossible to establish the ignition temperature as the partial pressure curve at -34 C is already within the lower explosive limit and ignition occurs immediately.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

All rooms in which work with nickel carbonyl takes place must be well equipped for intake and exhaust ventilation. A 30 to 40 times air change per hour appears to be sufficient. In the laboratories, under no conditions should more than a day's supply of nickel carbonyl be in storage. Organic solvents and other flammable fluids may not be kept or used in such rooms.

The in-plant storage (at nickel refineries) of liquid and gaseous nickel carbonyl utilizes alloy steel storage vessels sized for the particular refinery concerned (normally with a CO blanket). Recommendations for laboratory or small plant storage specify steel containers with a 2/5 ullage space filled with CO. The recommendations also specify that steel containers with nickel carbonyl must be stored upright in a special remote shed. The storage shed must be provided with the following essential capabilities: It must protect the contents against weather. The cylinders must be stored in cylinder racks. A functional air handling system, both intake and exhaust must provide for an optimal air movement in the room. A double roof should remove the excessive heat of the sun. The doors must be equipped with security locks. Warning plaques should advise of the danger of fire and poisoning. The storage area must be separated from the surroundings by a wall or fence, 5 meters distant. The storage area may be entered only with the knowledge of the person responsible and only with respiratory protective devices on. The responsible person is the keeper of the keys to the installation and is completely responsible for the enforcement of all safety measures. At least two persons must be participating whenever work in the storage area takes place. A third person must control the trace analyzer for nickel carbonyl. Before entry into the storage area, the exhaust fan must be working.

A complete inventory log must be kept on the fate of the stored amounts, including small quantities as well as large quantities which have been reworked into other materials or destroyed. The log must be complete and it has to describe the location, the time, and the manner in which the material was either used or destroyed.

The air in the room should be changed once every minute and the air in the glove box or similar confinement device should be changed 9 times per minute. Besides these general installations for ventilation of the room, the areas in which specially strong concentrations of nickel carbonyl could be expected such as the storage shed and the manifold

connections and gas drain valves should be equipped with special exhaust ducts. In these areas, respiratory protection devices for individual protection against nickel carbonyl should be used. The preferred device for respiratory protection is the self-contained oxygen breathing apparatus.

Special protective clothing is not considered necessary. Nickel carbonyl laboratory activities require normal laboratory coats made from cotton which in case of fire can be immediately removed from the body. Rubber gloves can be recommended for possible skin damage and perhaps absorption through the skin; however, nothing reliable is known about whether nickel carbonyl, besides the respiration danger, also carries the danger of penetrating skin in dangerous quantities. Therefore, the danger of percutaneous poisoning shrinks considerably in the background in view of the much greater danger of inhalation poisoning. The inhalation of nickel carbonyl is insiduous as there is no odor or (immediate) irritation of the respiratory organs.

The Department of Transportation (DOT) classification as a "flammable liquid, red label, not accepted for shipping" and the U. S. Coast Guard classification of "Inflammable Liquid, Red Label" are indicative of the hazard concerned. The recommended method of transport of small amounts of the material in steel containers is an open truck. The truck should be open with weather covering for the cylinders which are strapped in the vertical position. The truck should also be equipped with self-contained oxygen breathing apparatus, a resuscitator and CO_2 fire extinguishers.

Disposal/Reuse

As previously described, and demonstrated by an examination of the flowsheets (Figures 1 and 2) the primary process utilizing nickel carbonyl utilizes a complete recycle system. Nickel carbonyl is also inadvertently generated in many processes where CO passes over finely divided Ni. In these cases the small quantities generated are normally dissipated by increased ventilation. In other cases where small quantities of $Ni(CO)_4$ are generated as part of the process they are either regenerated in a

manner similar to that used for the recycling in the Mond process for the recovery of Ni or small quantities are burned to release Ni and CO. The particulate Ni is scrubbed from the gas stream and the CO is normally released from a tall stack to atmosphere so that normal atmospheric dispersion will reduce the concentration of CO to well below toxic levels. Known discharge of liquid nickel carbonyl into sewer systems is prohibited because of the extreme hazard of the vapors. The provisional limits for nickel carbonyl in the environment are:

Contaminant and Environment	Provisional Limit	Basis for Recommendation
Nickel carbonyl in air	0.00001 ppm (0.00007 mg/M^3)	0.01 TLV
Nickel carbonyl in water and soil	0.00035 ppm (mg/l)	Stokinger and Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

As described above, the present waste management practices fall into two categories:

(1) Recycle where large quantities of $Ni(CO)_4$ are utilized for extraction purposes.

(2) Thermal decomposition and wet scrubbing for disposal of small quantities.

Neither of these methods constitute a threat to the environment in a normal operating mode. In a recycle system, leakage from a portion of the system can normally be isolated until the operation can be shut down for repair. Decomposition heaters for small quantities are normally fitted with alarms in case the flame goes out.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The present methods for the handling and treatment of large quantities of nickel carbonyl are adequate. Only small quantities are found at any one place in the United States as the main producer of Ni (Hanna Mining, Riddle, Oregon) mines a laterite ore and does not use a nickel carbonyl process refining. However, because of the high degree of toxicity and hazards associated with $Ni(CO)_4$, it is recommended that National Disposal Sites be equipped to dispose of small quantities by thermal decomposition and wet scrubbing.

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HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. Name Nickel Carbonyl (293)

IUC Name Nickel Carbonyl

Common Names

Structural Formula

$Ni(CO)_4$

Molecular Wt. 170.73 Melting Pt. -25 C Boiling Pt. 43.2 C

Density (Condensed) S.G. 1.31 @ 25 C Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

261 mmHg @ 15 C 400 mm @ 25.8 C 760 mm @ 42.5 C

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower 3 Upper 43 *see comments

Solubility

Cold Water 0.018 g/100ml Hot Water -- Ethanol soluble

Others:

Acid, Base Properties Unreactive with aqueous acids and alkalies

Highly Reactive with Oxygen

Compatible with steel containers are used, synthetic rubbers are considerably more resistant than natural rubbers which harden

Shipped in steel containers under CO_2 blanket w/2/5 ullage

ICC Classification FL, Red Label, not accepted Coast Guard Classification 1L; red label

Comments Extremely toxic but decomposes readily with heat to Ni and CO - liquid colorless to straw yellow. Explosive limits: nickel carbonyl/air mixtures are ignitable and explosive in a wide range. It lies between 3 and 34 percent volume in air. Nickel carbonyl is auto-igniting at contact with oxygen in the air. Based on these properties it is impossible to establish the ignition temperature as the partial pressure curve at -34 C is already within the lower explosive limit and ignition occurs immediately.

References (1) 1570

(2) 0376

PROFILE REPORT

Perchloric Acid (To 72 Percent Strength) (324)

1. GENERAL

In its usual commercial form, 70 to 72 percent aqueous solution, perchloric acid has no oxidizing power when cold. Its properties are those of a strong acid. The cold 72 percent acid reacts with active metals with the liberation of hydrogen and formation of perchlorates. When heated, reduction of the perchlorate ion begins to take place and hydrogen chloride becomes a product. The lack of oxidizing power of cold perchloric acid permits the preparation of numerous organic salts of the acid thus establishing its wide use in the titration of organic bases in non-aqueous solvents. The hot, concentrated acid, however, is a strong oxidizing agent which makes it useful in analytical work for wet ashing organic matter and in the determination of chromium in steel.

Most commercial perchloric acid is made by the Permet Process in which sodium perchlorate is dissolved in water and reacted with an excess of concentrated hydrochloric acid to precipitate sodium chloride. The sodium chloride is filtered off to give a filtrate containing about 32 percent perchloric acid. The hydrogen chloride is boiled off, condensed and returned to react with additional sodium perchlorate. The dilute perchloric acid is then concentrated by evaporation to about 57 percent while any remaining hydrogen chloride is lost in the vapors which should be scrubbed. The crude perchloric acid is vacuum distilled in a glass or glass-lined still to produce a product of 70 to 71 percent perchloric acid. Sodium perchlorate crystals form as a waste product, but these are recovered and added to the sodium perchlorate used in the initial reaction.[1156]

The physical/chemical properties for perchloric acid are summarized in the attached worksheet.

2. TOXICOLOGY

Perchloric acid is considered only slightly toxic. However like other strong acids, perchloric acid in the form of liquid, mist or vapor is highly corrosive to the skin, eyes and mucous membranes. The amount of damage will depend upon the concentration, temperature, and duration of contact. Perchloric acid is considered to be a primary skin irritant. Since perchloric acid is not very volatile, the types of injury most likely to occur in industry are irritation of the respiratory tract through inhalation of the mist or spray, and severe burns of the eyes and skin through contact with the liquid.[0766, 1156]

When diluted and neutralized with sodium, potassium, or calcium hydroxides or carbonates, the perchlorate ion is slightly toxic. Oral doses of 200 to 400 mg of potassium perchlorate every 8 hr for periods up to 52 weeks were given to treat hyperthyroidism in humans. Other than a decrease in the serum concentration of protein-bound iodine, no significant changes in the subjects were noted.[1156]

Goldfish in water containing 0.1 percent sodium perchlorate were not affected; but when the sodium perchlorate concentration was raised to 0.2 percent, one in five fish died after 24 hr exposure.[1156]

3. OTHER HAZARDS

Anhydrous perchloric acid undergoes spontaneous explosive decomposition in storage, and will explode as the result of violent reaction with trace contaminants. For this reason anhydrous $HClO_4$ should not be prepared except in small quantities for research purposes, and anything which will dehydrate 72 percent $HClO_4$ should be avoided. Dehydration takes place upon vacuum distillation, and (explosively) on contact with concentrated H_2SO_4. Perchloric acid in excess of 72 percent concentration is prohibited from shipment and in some areas a special permit is required to prepare anhydrous perchloric acid. Even the aqueous solution of 72 percent

perchloric acid requires special precautions in its use. Contact of perchloric acid solution with easily oxidized or combustible materials or with dehydrating or reducing agents may result in fire or explosion. If used in wet combustion of organic material, the sample must first be treated with nitric acid to destroy easily oxidized organic matter.[0766, 1156]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Cold 72 percent perchloric acid reacts with active metals with the liberation of hydrogen and formation of the perchlorates. Marked passivity is noted in certain cases, e.g., iron, chromium and nickel. Only the platinum metals and glass are not attacked by hot perchloric acid limiting the materials of construction for equipment used in handling perchloric acid.

Perchloric acid, providing the concentration does not exceed 72 percent by weight, is classified by the U. S. Department of Transportation (DOT) for shipment as a corrosive liquid under a white Acid label. Perchloric acid solutions, in bottles having a capacity not over 1 lb or 16 oz by volume, enclosed in a metal can, are exempt from special packaging, marking and labeling requirements. Each box with larger inside containers and carboys must bear a white Acid label.[1156]

Waste streams containing perchloric acid must be neutralized to a pH of 6.5 to 9.2 before discharging into streams or lakes.[0536] The concentration of perchlorate ion discharged should not exceed 0.1g/100g of water.

The safe disposal of perchloric acid is defined in terms of the recommended provisional limits in the atmosphere, and in water and soil. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Perchloric Acid	0.01 mg/M^3	Based on similar compounds

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Perchloric Acid	0.05 ppm	Based on similar compounds

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

The recommended disposal procedure by the Manufacturing Chemists Association for packaged lots of perchloric acid is to add the acid to a large volume of a reducer such as sodium thiosulfate, a bisulfate or a ferrous salt acidified with 3M-H_2SO_4.[0095] The reported reduction takes place when the solutions are heated. The reduction of perchloric ion to chloride with heated ferrous sulfate is recommended for use with extreme care. The reduction products must be tested to determine that complete reduction of the perchlorate ion has occurred.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

It is not anticipated that large quantities of aqueous perchloric acid solutions (up to 72 percent in concentration) will require disposal. However, because of the hazards associated with the destruction of perchloric acid, treatment of excess or waste perchloric acid at National Disposal Sites is recommended. The process recommended is the hot reduction with ferrous sulfate and dilute sulfuric acid.

7. REFERENCES

0095. Manufacturing Chemists Association. Laboratory waste disposal manual. 3d ed. Washington, Manufacturing Chemists Association, 1970. 176 p.

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HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. Name Perchloric acid (324)

IUC Name Perchloric acid

Common Names

Structural Formula

$HClO_4$

Molecular Wt. 100.47(1) Melting Pt. -112 C(1) Boiling Pt. 16 C(8 torr)(1)

Density (Condensed) 1.764 @ 20 C(1) Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water soluble(1) Hot Water soluble(1) Ethanol soluble(1)

Others: acetic acid, most polar organic solvents - soluble(1)

Acid, Base Properties strong acid(1)

Highly Reactive with Reducing substances and active metals(1)

Compatible with

Shipped in Glass bottles 1 and 5-lb, carboys 2,5 and 10-gal(1)

ICC Classification corrosive liquid, white label(1) Coast Guard Classification Corrosive liquid, White Label (1)

Comments Forms constant boiling mixture containing 71.6 percent acid.

References (1) 1156

PROFILE REPORT

Acrolein

1. GENERAL

Acrolein is a clear, colorless, volatile liquid, soluble in many organic liquids; it is a powerful lacrimator and is highly toxic. It is also one of the most reactive organic chemicals available to industry. The extreme chemical reactivity of acrolein is attributed to the conjugation of a carboxylic group with the vinyl group within its structure. Because of its toxic nature and because both the liquid and the vapor are flammable, acrolein must be handled with extreme care.[1317,1434]

Acrolein is manufactured on a commercial scale by the direct oxidation of propylene or by the cross-condensation of acetaldehyde with formaldehyde.[1433] It is used in the manufacture of pharmaceuticals, amino acids, odorants, dyestuffs, textile finishing resins, paper chemicals, polyesters, and polyurethanes.[1317]

Large scale commercial facilities for the manufacture of acrolein are operated by Union Carbide Chemicals and Shell Chemical Corporation.[1434] Physical/chemical properties are summarized in the attached worksheet.

2. TOXICOLOGY[1317]

Acrolein is a highly toxic chemical and is poisonous by ingestion, inhalation, and absorption through the skin. It is intensely irritating to the eyes, respiratory tract, and lungs and should be handled only in a closed system or under conditions that provide ample ventilation.

Exposure to one part per million of acrolein in air produces detectable eye and nose irritation in 2 or 3 min., moderate eye irritation with lachrymation in 4 min and is tolerable in 5 min.[1433] The Threshold Limit Value (TLV) quoted in the current Occupational Safety and Health Standards (Fed. Reg. 1971) of 0.1 ppm is sufficiently low to minimize, but not entirely prevent, irritation to all exposed individuals. The TRW assessment of the toxicological information recommends a limit in air of 0.001 ppm (0.0025 mg/M^3) for 24 hr exposure.

The liquid can be absorbed through the skin causing severe burns. It also causes severe burns to the eyes. Care should be exercised in handling to prevent contact of the liquid with the skin, eyes, or clothing.

3. OTHER HAZARDS

Acrolein monomer is a dangerous substance due to its flammability and high reactivity. The explosive limits in air are between 2.8 and 31 percent by volume of acrolein. Inadequately inhibited acrolein may also be subject to explosive polymerization.[1433] For this reason, it is shipped under an oxygen-free atmosphere and inhibited with hydroquinone.[1317]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage and Transportation

Special methods of handling and storage of acrolein are required. Preferably, all processing equipment, as well as storage facilities should be located outdoors to afford adequate ventilation. All electrical equipment, motors, lights, and flashlights used in an area in which acrolein is handled should be vapor tight or explosion proof. Static electricity should be guarded against by properly grounding all equipment, tanks, piping, loading racks, etc.[1317] Iron and steel are satisfactory materials of construction for handling inhibited acrolein. Copper metal or its alloys is recommended in distillation systems because of the additional inhibiting effect conferred by these materials.[1434]

Suitable storage and handling facilities should be available to keep acrolein under an oxygen-free atmosphere since inadequately inhibited acrolein is subject to explosive polymerization.[1433] It is recommended that any appreciable quantity of acrolein be stored or handled in a non-draining, diked area in order to confine this very toxic chemical in the event of spillage.[1317] For large scale operations, workers should wear protective equipment such as glasses and gas masks.[1433] Shipping regulations are found in the Code of Federal Regulation 49CFR73.122 for 1-gal. containers (2A), 55-gal. drums (5A) and 6- and 10-thousand-gallon tank cars (105A-500).

Disposal/Reuse

Criteria for the disposal of acrolein in waste aqueous streams must take into account the products formed during neutralization of these dilute (parts per billion) solutions. The reaction with the carbon-carbon double bond is catalyzed by base.[1434]

Current techniques[1318] utilize neutralization of the acrolein with base and lagooning (secondary treatment). Low molecular weight oligomers containing hydroxyl and aldehyde functionalities are formed in base catalyzed reactions.[1451] These structures are generally biodegradable.[0314] The waste acrolein streams are too dilute to be amenable to incineration, therefore, secondary treatment or deepwell disposal is presently used.

Acrolein appears as an organic waste stream constituent in varied forms and compositions. A typical organic liquid waste stream (generated in the petrochemical industry) containing acrolein has the following composition:

Light naphtha containing 1 to 5 percent acrolein; up to 5 percent acrolein dimers and trimers.

Information relating to the quantities of acrolein containing wastes generated annually is presented in Volume XIV "Waste Forms, and Quantities".

Recommended provisional limits for acrolein in effluent streams released to the environment from acrolein waste disposal processes are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Acrolein	0.001 ppm (0.0025 mg/M^3)	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Acrolein	0.01 ppm (mg/l)	Stokinger & Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Acrolein appears primarily as aqueous waste streams in low concentrations and only rarely as concentrated waste. The processing options are briefly described in the following paragraphs together with recommendations as to their adequacy.

Concentrated Acrolein

In the event it becomes necessary to dispose of a significant quantity (55-gal. drum or 10,000-gal. tank car) of concentrated acrolein, two disposal options are available. The first option is to contact the manufacturer and determine if it is possible to return the material. Union Carbide Corporation[1418] has indicated a willingness to accept concentrated acrolein for reprocessing. The second option is incineration since acrolein is highly flammable and amenable to this treatment. In fact, many plants using this material maintain incinerators for disposal of combustible liquid byproducts and these same facilities can and are used to dispose of waste acrolein.[1418] It is expected that any liquid combustion unit operated at a minimum temperature of 1,500 F (0.5 seconds minimum residence time) followed by secondary combustion at a minimal temperature of 2,000 F for 1.0 second would completely convert acrolein to carbon dioxide and water. Complete combustion of acrolein would not require subsequent scrubbing of the combustion products. Both options present adequate ways to handle the concentrated waste but it is strongly urged that all possible effort be directed toward recycling the material and that incineration be used only as a back-up option.

Dilute Aqueous Waste

Acrolein appears as waste in water at concentrations in the order of parts per billion in the manufacturing process.[1431] Other sources of waste are from water used in the cleaning of equipment used in acrolein service.[1317] Methods for adequately handling the disposal of dilute aqueous solutions of acrolein are currently under study by Union Carbide Corporation under the partial sponsorship of EPA.[1318]

Option No. 1 - Secondary Treatment. Secondary treatment procedures comprised of neutralization and subsequent lagooning are currently being used by Union Carbide Corporation.[1318] Sufficient information is not available at this time to make a recommendation as to its adequacy.

Option No. 2 - Deepwell Disposal. Although deepwell disposal is currently utilized as a means of dilute aqueous acrolein waste disposal, the method is judged to be inadequate. This judgement is based primarily on three factors. First, the problem of assuring that a deepwell will operate satisfactorily over a long period of time is extremely complex and costly, and therefore proper methods of assurance are seldom followed. Secondly, there has been little research in the area of long term effectiveness of this form of disposal and thirdly, deepwell injection really represents a form of relatively unaccessable long-term storage for most organic materials, as opposed to conversion to a nonhazardous material. Currently utilized deep well disposal methods are described by Jones.[0314] A general description of the technique is given in Volume III.

Option No.3 - Combustion. Submerged combustion is a direct combustion method used by the petrochemical industry. A specially designed burner has been used successfully for total or partial evaporation of waste streams and for concentrating dissolved solids.[0314] A detailed description of the Fredrich Uhde Combustion Process and the Fluor Submerged Combustion Process has been provided by Jones.[0314] The concentrated effluent from this process may then be treated as a concentrated waste as discussed in the section on Concentrated Acrolein of this report. In principal, this means of dilute waste treatment should be adequate.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Due to its extreme chemical reactivity, toxicity, flammability, and the processing difficulties associated with those characteristics, it is anticipated that disposal systems to handle both dilute and concentrated acrolein wastes will be required at National Disposal Sites located near manufacturers and users. The dilute acrolein wastes that will require treatment include spent cleaning solutions for acrolein containers and any other on-site generated waste water containing acrolein. The concentrated acrolein wastes that will require treatment include any surplus, contaminated, or degraded material.

The processes recommended for the treatment of dilute acrolein wastes at National Disposal Sites are:

Process	Order of Preference	Remarks
Biological	First Choice	In principal, this method appears adequate when followed by proper disposal of the concentrated effluent.
Submerged Combustion	Second Choice	Method currently used; effectiveness currently under study; requires neutralization prior to lagooning.

The process for treatment of concentrated acrolein wastes at National Disposal Sites are:

Process	Order of Preference	Remarks
Recycle	First Choice	Major producer has indicated willingness to accept concentrated acrolein waste.
Incineration	Second Choice	Demonstrated technology; applicable to most organic wastes.

7. REFERENCES

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1451. Gilbert, E. E., and J. J. Donleavy. The polycondensation of acrolein. Journal of the American Chemical Society, 60(2):1,911-14, Aug. 1938.

HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. Name ACROLEIN (8)

C_3H_4O

IUC Name 2-propenal

Structural Formula

CH_2:CHCHO

Common Names Acrolein, propenol; acrylic aldehyde

LC_{50} mice 66 ppm for 6 hrs.

TLV 0.001 ppm (0.0025)/24 hrs.

Molecular Wt. 56.06[1] Melting Pt. -87.7 C[1] Boiling Pt. 52.5 C[1]

Density (Condensed) 0.841 @ 20 /4 C[1] Density (gas) 1.44 @ ____

air = 1.0

Vapor Pressure (recommended 55 C and 20 C)

N_D^{20} 1.4013

760 mm @ 52.5 C[1] 215 mm @ 20 678.5 mm @ 50

Flash Point ____ Autoignition Temp. 532 F[1]

Flammability Limits in Air (wt %) Lower ____ Upper ____

Explosive Limits in Air (vol.%) Lower 2.8 Upper 31

Solubility

Cold Water 20.8% (wt) at 20 C Hot Water 24.0% (wt.) Ethanol Soluble

Others: Soluble in ether

Acid, Base Properties Approx. Neutral

Highly Reactive with Highly flammable; subject to explosive polymerization

Compatible with Acetic acid (as inhibitor); Hydroquinone as inhibitor

Shipped in Iron, Steel, Copper, Metal

ICC Classification 28, 29 Coast Guard Classification Flammable[1]

Comments Mfg. : Shell Chemical Co.; Union Carbide Corp. Chemical & Plastics

References (1) 0766

PROFILE REPORT

Dimethyl Sulfate (160)

1. GENERAL

Dimethyl sulfate is an extremely toxic, colorless, oily liquid. This material is particularly hazardous because it has no characteristic odor or other warning property and symptoms of exposure to the vapors or liquid often do not appear for several hours after the event.[1492] It is readily hydrolyzed by water to form corrosive sulfuric acid.

The principal domestic manufacturer of dimethyl sulfate is E. I. du Pont de Nemours, Inc.,[1571] who probably produce it from dimethyl ether and sulfur trioxide.[1492] It is used as a reagent for the introduction of methyl groups (methylating agent) in the manufacture of many organic chemicals.

The physical/chemical properties of dimethyl sulfate are summarized in the attached worksheet.

2. TOXICOLOGY [1492,0766]

The use of dimethyl sulfate as a war gas is testimony for the hazardous nature of this compound. The most dangerous property of this material is its virtual lack of warning characteristics (e.g., odor, irritation) and the delayed appearance of symptoms which may permit unnoticed exposure to lethal quantities.

The liquid produces severe blistering and necrosis of the skin. Sufficient skin absorption can occur to give serious poisoning. Dimethyl sulfate vapors, after a latent period of several hours, cause severe inflammation and necrosis of eyes, mouth and respiratory tract resulting in pulmonary damage. Systemic effects may include prostration, convulsions, delirium, paralysis, coma and delayed damage to kidneys, liver and heart. Death may occur in three or four days in cases of heavy exposure.

A Threshold Limit Value (TLV) (skin) of 1 ppm or 5 mg/M^3 has been recommended for man.[1493] Dimethyl sulfate is also extremely toxic to other species. The LD_{50} (oral) in rats has been reported [1492] to be 440 mg/kg and the fatal concentration for cats and monkeys is in the range of 25 to 200 ppm of the vapor in the air.[0766]

3. OTHER HAZARDS

Dimethyl sulfate hydrolyzes in the presence of water to form sulfuric acid and methanol. A concentrated solution of sulfuric acid is extremely corrosive to many materials and will react exothermically with bases. Explosive reactions have been reported [1569] for mixtures of dimethyl sulfate with ammonium hydroxide and with sodium azide.

Dimethyl sulfate will burn at temperatures above its flash point, but under normal handling conditions there is little danger of fire.[1493,0766]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Detailed procedures for the safe handling, storage and transportation of dimethyl sulfate may be found in the MCA Safety Data Sheet SD-19.[1493] The governing principle for the safe handling of dimethyl sulfate is the scrupulous avoidance of any contact with liquid or vapor. The effectiveness of the methods and equipment designed for this purpose [1493] will depend primarily on the effectiveness of employee education in their use.

Dimethyl sulfate is shipped in glass bottles and steel containers as large as tank cars.[0766] It is classified by the Department of Transportation and U. S. Coast Guard as a corrosive liquid, requiring a white label.[0766] It is considered unacceptable for shipment by air on passenger flights and is limited to one liter containers on all-cargo flights.

Disposal Reuse

Dimethyl sulfate may be purified by distillation at reduced pressure; distillation at normal atmospheric pressure results in decomposition.[1492] The dangers inherent to the handling of a material with the insidious characteristics of dimethyl sulfate militate against the purification for reuse of large quantities of the material by any but the most experienced personnel.

An adequate process for the disposal of dimethyl sulfate must include, as the first step, dilution with water to less than one percent concentration.[1493] Dilution reduces the danger of accumulation of toxic quantities and hydrolyzes the dimethyl sulfate to sulfuric acid and methanol. The diluted solution should then be neutralized with base to reduce its corrosive nature.

Recommended provisional limits for dimethyl sulfate in the environment are as follows:

Contaminant and Environment	Provisional Limit	Basis for Recommendation
Dimethyl Sulfate in Air	0.01 ppm or 0.05 mg/M^3	0.01 TLV
Dimethyl Sulfate in Water and Soil	0.25 ppm (mg/l)	Stokinger and Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

The preferred processing options for the disposal of dimethyl sulate wastes are briefly described in the following subsections together with judgements as to their adequacy.

Option No. 1 - Incineration

The Manufacturing Chemists Association (MCA) recommends that dimethyl sulfate be disposed of by incineration in properly designed and operated chemical waste incinerators.[1493] The MCA also recommends that the waste be diluted and neutralized before disposal, whenever conditions permit.[1493]

Incineration of dilute (1%), neutralized dimethyl sulfate waste is recommended as the best method for disposal of the material. The incineration must be performed by trained and experienced personnel using equipment properly designed to handle hazardous materials and equipped with efficient oxides of sulfur scrubbing devices. These incinerators should expose the waste material to a minimum temperature of 1,800 F for at least 1.5 seconds. These conditions may be easily met through the use of afterburners. Disposal of concentrated dimethyl sulfate wastes by direct incineration is judged to be less acceptable for all but very small (laboratory) quantities of material. The danger of exposure to vaporized, but unburned dimethyl sulfate is significantly greater when the material is disposed of in concentrated form and, therefore, requires the employment of specially trained personnel operating properly designed and maintained equipment.

Option No. 2 - Waste Water Treatment

The use of biological waste water treatments methods for the disposal of dimethyl sulfate are acceptable only for very dilute, neutralized waste streams. These procedures are less satisfactory than proper incineration because of the danger of exposure to incompletely hydrolyzed dimethyl sulfate.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Dimethyl sulfate is judged to be a candidate waste stream constituent for disposal at National Disposal Sites. The high toxicity and insidious nature of this material will require careful handling by trained and experienced personnel using well designed and maintained equipment. Assurance that the criteria for the safe disposal of dimethyl sulfate are met can best be obtained at a facility specializing in the handling of such difficult materials.

It is recommended, for the reasons outlined in Section 5, that incineration of dilute, neutralized dimethyl sulfate wastes be the disposal method used at National Disposal Sites.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Dimethyl Sulfate (160)

IUC Name Sulfuric acid, Dimethylester

Common Names (1) Methyl Sulfate, DMS

Structural Formula

$(CH_3O)_2\ SO_2$

Molecular Wt. 126.13 Melting Pt. -31.75 C Boiling Pt. 188.5 C (d)

Density (Condensed) 1.3283 @ 20C/20C Density (gas) 4.35 @ (Air=1) _____

Vapor Pressure (recommended 55 C and 20 C)

15mm @ 76 C (2) _____ @ _____ _____ @ _____

Flash Point (1) 83.3 C (cc) Autoignition Temp. _____
115.6 C (oc)

Flammability Limits in Air (wt %) Lower _____ Upper _____

Explosive Limits in Air (wt. %) Lower _____ Upper _____

Solubility (3)

Cold Water 2.8 g/100ml @ 18 C Hot Water Hydrolysis Ethanol soluble

Others: ether, dioxane, acetone, aromatic hydrocarbons

Acid, Base Properties Neutral when anhydrous, hydrolyses rapidly in water to yield H_2SO_4

Highly Reactive with Ammonium hydroxide, (4) Sodium Azide, (4) Oxidizing materials (5)

Compatible with (1) Glass, stainless steel (in the absence of moisture)

Shipped in (1) Glass bottles, steel drums and tank cars

ICC Classification Corrosive Liquid, white label Coast Guard Classification (5) Corrosive liquid White label

Comments IATA classification: corrosive liquid, white label, not acceptable (passenger), 1 liter (cargo). (5) Source: DuPont (6)

References (1) (1493) (4) (1569)
(2) (1570) (5) (0766)
(3) (1492) (6) (1571)

PROFILE REPORT

Pentachlorophenol (322)

1. GENERAL

Pentachlorophenol is a broad-spectrum biotoxicant available commercially in the form of flakes and needle crystals. Because of its high toxicity, it is also available in a prilled form and oiled grade to greatly reduce dust associated with the flakes and needles.[1433] The pure material melts at 191 C and decomposes at 310 C.[0766]

Pentachlorophenol can be manufactured by the direct chlorination of phenol and polychlorophenols. One commercial process[1433] uses a mixture of phenol, o-chlorophenol,2,6-dichlorophenol, and 2,4,6-trichlorophenol as the starting materials. Chlorination is carried out in the absence of solvents and catalyst until tetrachlorination is achieved; at that point a Lewis acid catalyst such as $FeCl_2$, $AlCl_3$, $SbCl_3$, etc., is added to facilitate the incorporation of the fifth chlorine group. The progress of the reaction is monitored by determining the freezing point of the product. When the proper freezing point is achieved, the chlorinatior is stopped, and the material is flaked and packaged. Pentachlorophenol is also manufactured by the hydrolysis of hexachlorobenzene[1433] with 5 to 15 percent sodium hydroxide in methanol at 130 to 140 C. The hexachlorobenzene is easily prepared by the liquid-phase, iron-catalyzed chlorination of benzene.

The textile industry uses pentachlorophenol to preserve rope, binder twine, burlap, cable covering and rubberized canvas belting. It is also utilized by the wood and construction industries to impart termite resistance to wood and to control mold growth on lumber products and building surfaces. The pentachlorophenol is generally incorporated in the treating of materials such as whitewash or paints, or mixed with oil for spray application. It also finds use in the leather industry to impart temporary mold resistance to upper leather for shoes,[1512] and as a fungicide and herbicide.[1277]

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Domestic production of pentachlorophenol was reported as 47.2 million pounds while the quantity sold was 45.8 million pounds for the year 1970, the remainder being for captive use. Manufacturers of pentachlorophenol are Dow Chemical Company, Monsanto Company, Reinhold Chemicals Inc., Sanford Chemical Company, and Vulcan Materials Company.[1718]

2. TOXICOLOGY[1512]

Pentachlorophenol is capable of producing severe irritation and corneal damage upon contact with the eye. A single short exposure to the skin may cause some reddening, while repeated or prolonged contact may cause severe irritation or burns. This material is readily absorbed through the skin in toxic amounts, particularly from solutions, and is highly toxic if swalloed. Dust concentrations which are hazardous are very irritating to the nose and throat. The material is not likely to cause sensitization nor should there be any problem from ingestion incidental to correct industrial handling.

The Threshold Limit Value (TLV) and maximum allowable concentration[0766] is 0.5 mg/M^3. LD_{50} for rats is 125-210 mg/Kg orally and 150-350 mg/Kg dermal.[1277]

3. OTHER HAZARDS

Although pentachlorophenol has no fire or flash point, it is dangerous when heated to decomposition. Decomposition takes place at 310 C with the emission of highly toxic fumes of chlorides.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation[1512]

Safety glasses with side shields, or their equivalent, should be worn when this material or its solutions are handled. Where the likelihood of appreciable exposure to dust or strong solutions cannot be avoided, workers

should wear appropriate protective devices, including underwear with full length arms and legs, coveralls, or other outer garments covering the whole body, cloth gloves, cap, and a dust respirator bearing the approval of the U. S. Bureau of Mines for use with toxic dusts. Impervious sleeves with elastic bands at either end, to fit over long gauntlet gloves, may be useful for protecting the arms and wrists. For extensive manual operation it may be necessary to utilize protective rubber gloves.

Disposal/Reuse

A definition of acceptable criteria for the disposal of pentachlorophenol must also take into account acceptable criteria for the release of hydrogen chloride and hydrochloric acid to the environment, since current practice in pentachlorophenol disposal involves some processes that reduce pentachlorophenol to these materials.

Any method of safe disposal of this material must insure that the concentration of pentachlorophenol, hydrogen chloride and hydrochloric acid in the environment does not exceed the following recommended provisional limits:

Contaminant and Environment	Provisional Limits	Basis of Recommendation
Pentachlorophenol released to the atmosphere	0.005 mg/M^3	0.01 TLV
Hydrogen chloride released to the atmosphere	0.05 ppm (0.07 mg/M^3)	0.01 TLV
Hydrochloric acid released to the atmosphere	0.05 ppm (0.07 mg/M^3)	0.01 TLV
Pentachlorophenol in water	0.25 ppm (mg/l)	Stokinger and Woodward

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Little information is available from literature and industrial sources pertaining to the disposal of pentachlorophenol waste streams. However, pentachlorophenol is chemically and structurally similar to other chlorophenoxy compounds such as 2,4-D (2,4-dichlorophenoxy acetic acid), 2,4,5-T (2,4,5-trichlorophenoxy acetic acid), and MCPA (2-methyl-4-chlorophenoxy acetic acid), and it is therefore assumed that processes applicable to those wastes are applicable to pentachlorophenol wastes. The various processes for treating concentrated and dilute chlorophenoxy waste streams are discussed in detail in the Profile Report covering 2,4-D (135). The salient points of those discussions are presented in the following sections of this report.

Dilute Pentachlorophenol Wastes

Option No. 1 - Adsorption with Powdered Activated Carbon. The addition of powdered activated carbon to dilute aqueous waste streams followed by stirring and filtration has proven to be an adequate method of low concentration chlorophenoxy compound removal. Studies have shown that compounds such as 2,4-D and probably pentachlorophenol can be removed with as high as 99 percent efficiency under certain processing conditions (carbon dosage of 320 mg/liter, a pH of 6, and one hour contact time as in the case of a 10 ppm 2,4-D waste stream). The carbon adsorbent may then be collected for disposal or the pentachlorophenol may be removed in rotary hearth incinerators equipped with hydrogen chloride scrubbers. The activated carbon may then be recycled.

Option No. 2 - Adsorption with Granular Activated-Carbon Beds. This method of treatment has been successfully utilized to treat wastewater containing 2,4-D and 2,4,5-T with removal efficiencies as high as 99 percent. The concentrated chlorophenoxy compounds are removed from the carbon adsorbent through controlled oxidation in rotary hearth

incinerators with subsequent effluent scrubbing to remove chlorides. Because the technology is proven and since it is a well established chemical engineering unit operation, adsorption with granular activated-carbon beds should be considered as one of the more satisfactory methods for treating dilute pentachlorophenol wastes.

Option No. 3 - Biological Degradation. Biological degradation of dilute waste streams containing dichlorophenol has been utilized. One such process started with pretreatment of the waste stream by first sending it through a crushed limestone filled neutralization ditch and an in-plant equalization pond, and a final pH adjustment to 7.2 by automatic addition of slaked lime slurry in a continuous stirred pit. The wastewater, containing 2 to 4.2 mg/liter phenoxy acids, was then treated in an aerated lagoon and stabilization pond system before discharge to a receiving stream. Although the removal of chlorophenoxy acids by the lagoon and pond system ranged from only 49 to 80 percent, the stabilization pond effluent with typically 1.1 mg/liter chlorophenoxy acids was considered to be good quality. This would indicate that streams containing pentachlorophenol (instead of dichlorophenol) could possibly be biologically treated, however more work needs to be done in this area to establish proper processing parameters.

Option No. 4 - Ion Exchange. The use of ion exchange columns to remove chlorophenoxy compounds such as the sodium salt of 2,4-D from water has been examined. It was determined that when chlorophenoxy compounds are neutralized to their sodium salts, that ion exchange can remove concentrations as high as 120 mg/liter completely using strongly basic anion resins. It would appear that ion exchange is an adequate method for treating dilute pentachlorophenol wastes.

Concentrated Pentachlorophenol Wastes

Option No. 1 - Incineration. The complete and controlled high temperature oxidation coupled with adequate scrubbing and ash disposal facilities offers the greatest immediate potential for the safe disposal

of concentrated pentachlorophenol. The research on incineration of pestcides conducted by Kennedy et al at Mississippi State University has led to the conclusion that chlorophenols approach complete oxidation when combusted at temperatures in the 600 C to 900 C range with hydrogen chloride being the only pollutant liberated. If proper aqueous or caustic scrubbing systems are utilized, efficient abatement of the hydrogen chloride can be achieved. Therefore, properly designed and operated incination is considered the best present and near future method for the disposal of concentrated pentachlorophenol.

Option No. 2 - Deep-Well. Although pentachlorophenol is only sparingly soluble in water, its persistence and stability in water and the potential contamination of ground water make deep-well at best a questionable method for disposal. The method is not recommended by the National Working Group on Pesticides, and should not be considered.

The disposal of pentachlorophenol wastes as well as other chlorophenoxy wastes in open pits, lagoons, unapproved landfill sites, by application to the soil surface, and by on site burning or deep sea burial are not recommended practices because of the obvious potential contributions to air and water pollution.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

It is anticipated that disposal systems to handle both dilute and concentrated pentachlorophenol and similar compounds will be required at National Disposal Sites located near manufacturers, users, and especially agriculture centers in the near future. The dilute pentachlorophenol wastes that will require treatment include spent cleaning solutions from pentachlorophenol containers and any other contaminated wastewater. The concentrated pentachlorophenol wastes that will require treatment include any surplus, contaminated or fully degraded material.

The processes recommended for the treatment of dilute pentachlorophenol wastes at National Disposal Sites are:

Process	Order of Preference	Remarks
Activated-Carbon Beds	First Choice	Proven technology on commercial scale; also adequate for removal of the sodium salt of pentachlorophenol and most other types of pesticides from wastewater.
Ion Exchange	Second Choice	Demonstrated technology; requires preliminary conversion to the sodium salt.
Biological	Third Choice	Demonstrated technology on closely related compounds; requires treatment in aerated lagoons and stabilization ponds.

The processes for the treatment of concentrated pentachlorophenol wastes at National Disposal Sites are:

Process	Order of Preference	Remarks
Incineration	First Choice	Demonstrated technology; applicable to the disposal of most organic wastes; possibility of recovering chlorine in the form of usable hydrogen chloride.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. Name Pentachlorophenol

IUC Name Pentachlorophenol

Common Names Pentachlorophenol, Penta, Santophen 20, Dowicide 7

Structural Formula

C_6Cl_5OH

Molecular Wt. 266.35 (1) Melting Pt. 190 C (1) Boiling Pt. 310 C (decp) (1)

Density (Condensed) 1.978 @ 22/4 C (2) Density (gas) _____ @ _____

Vapor Pressure (recommended 55 C and 20 C)

5.5 @ 160 C (3) 50 @ 220 C (3) 550 @ 300 C (3)

Flash Point None (3) Autoignition Temp. _____ Fire point - none (3)

Flammability Limits in Air (wt %) Lower _____ Upper _____

Explosive Limits in Air (wt. %) Lower _____ Upper _____

Solubility

Cold Water Almost insoluble (1) Hot Water _____ Ethanol Freely soluble (1)

Others: Freely soluble in ether (1), soluble in benzene (1)

Acid, Base Properties Acidic, pK_a = 4.86 (1)

Highly Reactive with _____

Compatible with _____

Shipped in Multiwall paper bags (3), fiber drums (3)

ICC Classification _____ Coast Guard Classification _____

Comments LD_{50} orally in rats: 180 mg/Kg (1) MAC: ACGIH: 0.5 mg/M (3) of air

References (1) 1492 (4) 1433
(2) 1570
(3) 1512